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SPECULATION ON RECOVERY OF RUBIDIUM—86 FROM CLAYS

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Pilot investigations on the retention of NH_4^+ by soils indicated that the dominant clay mineral in a Merrimac sandy loam soil did not collapse from 14 Å to 10 Å on saturation with K^+.[2,3] Following a suggestion by Walsh and Murdock that organic matter could occupy space between 2:1 lattice-type clay minerals, a concurring premise was advanced that aside from possible interstratification with mica-vermiculitic materials, interlayer materials were present in the clay of the Merrimac soil.[4] It was speculated that the interlayer organic matter might interfere with the collapse of the clay mineral and NH_4^+ or K^+ fixation would be correspondingly decreased. Hanway et al. in 1955 indicated ample evidence for a reciprocity between K^+ and NH_4^+ in fixation by clay minerals.[5] Lattice distortions of organic-clay complexes have also been investigated by Weiss and Brunton et al.[6]

Clay fractions were obtained by sedimentation from Merrimac sandy loam and Suffield clay loam soils using Stoke's law.[7] Water was evaporated from resulting clay suspensions at temperatures of 100° C. Clays of both soils were identified as predominantly vermiculite or interstratified vermiculite.[3] Nine to one ratios of washed, fine-sea sand to respective clays were prepared. Twenty-five g. samples were mixed with 20 ml. of deionized water to form a slurry. Excessive amounts of finely-ground, potato-plant tissue (0.23 g.) and NH_4Cl (1.2 g.) were added to some slurries, stirred frequently, and allowed to equilibrate 24 hours. Rb^{86} was then added, 10uc/ml, followed by stirring intermittently for one hour, then incubation for 50 hours at room temperature. Control slurries consisted of those which received no imposed treatment and those which received only Rb^{86} Procedures of Dharival and Stevenson for the determination of fixed NH_4^+ were used to partition Rb^{86} into

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[1] Professor of Soil Chemistry and Research Graduate Assistant, respectively.

[2] Maine Progress Report, Contributing Project Northeastern Regional Nitrogen Research Project—NE-39. December, 1960.

[3] Clay mineral analyses conducted by Soil Survey Laboratory, Plant Industry Station, Beltsville, Maryland, Drs. L. T. Alexander, J. Cady, R. C. Van den Heuvel; and Department of Agronomy, Pennsylvania State University, University Park, Dr. R. P. Matelski. 1960 and 1961.

[4] Walsh, L. M., and Murdock, J. T. Native fixed ammonium and fixation of applied ammonium in several Wisconsin soils. Soil Sci. 89:183-193. 1960.

[5] Hanway, J. J., Scott, A. D., and Stanford, G. Replaceability of ammonium fixed in clay minerals as influenced by ammonium or potassium in the extracting solution. Soil Sci. Soc. Amer. Proc. 21:29-34. 1957.

[6] Eleventh Clay Mineral Conference, Program and Abstracts, Ottawa, Canada, pp. 15-16. 1962.

three fractions: first, water soluble; secondly, "adsorbed" fraction—simmered on hot plate for six hours with 1 N KOH; and thirdly, "fixed" or interlattice—treated with HF solution for 12 to 16 hours with occasional stirring.[8] Radioassays were made at the 5% error rate on two aliquots of respective filtrates from duplicate samples.

Results shown in table 1 indicate that the clay minerals from both soils generally responded the same to treatment. In the water-soluble fraction, pretreatment with NH_4^+ as NH_4Cl apparently partially saturated the exchange sites and resulted in the largest recovery of Rb^{86} The addition of plant material to the Suffield clay but not the Merrimac clay slurries resulted in a higher percentage of recovery of water soluble Rb^{86} compared with those which received no treatment with plant material prior to the addition of Rb^{86}. Theoretically, amorphous coatings of plant material may have blocked some exchange sites on the Suffield clay which could have been occupied by Rb^{86}; or conversely, it might be argued that pretreatment with plant material could have increased the cation exchange capacity. With the Merrimac soil, the recovery of "adsorbed" Rb^{86} was highest for the sedimented clay minerals when plant material was added prior to Rb^{86} which would tend to substantiate the theory of increased cation exchange. In refutation, however, recoveries of "adsorbed" Rb^{86} from the Suffield clay were essentially alike for no pretreatment and for pretreatment with plant material. Most significantly, the addition of plant material appeared to reduce the interlattice amounts of Rb^{86} in the filtrate of the fraction treated with HF solution. As noted, for example, in table 1, the Suffield clay had an Rb^{86} recovery rate of 14.8% when plant material was added; whereas, the rate was 29.2% when only Rb^{86} was used. The same trend occurred with the Merrimac clay. The lowest recovery of "fixed" Rb^{86} was present when clays were pretreated with NH_4Cl. Ammonium ions might be expected to collapse the lattice structure of the clays thus blocking the entry of Rb^{86}. It also seems apparent that the Merrimac clay "fixed" more Rb^{86}, 46.9%, than the Suffield clay, 29.2%. This might indicate that the interstratification of their minerals differed and the lattice structure of the Merrimac clay was collapsed to a greater extent by Rb^{86} than the Suffield clay. From a practical viewpoint, one might, therefore, expect the Merrimac clay to fix more NH_4^+ than the Suffield clay.

Since the valences of NH_4^+ and Rb^{86} are alike and their ionic radii are essentially the same, 1.4 to 1.5 Angstroms,[9] it might be assumed that Rb^{86} could be used to evaluate the retention of NH_4^+ and K^+ by clay minerals or soils. Thence it is interesting to speculate and con-

[7] Baver, L. D. Soil Physics. John Wiley and Sons, Inc. New York, Ed. 3, pp. 55-56. 1956.

[8] Dharival, A. P. S., and Stevenson, F. J. Determination of fixed ammonium in soils. Soil Sci. 86:343-349. 1958.

clude analogously that pretreatment of clay slurries with plant material resulted in interlayer organic matter which would restrict the entrance or interlattice "fixation" of these ions, since the interlayer amounts of Rb^{86} appeared to be reduced. To appropriately substantiate this premise, however, considerations need to be given to effects of Rb^{86} on lattice expansion and collapse of clays and to correlation studies of Rb^{86} recovery data with X-ray diffraction patterns.

[4] U. S. Rubber Company, Handbook of Chemistry and Physics, 44th Ed., p. 3507. 1962.

TABLE 1. Effects of pretreatment with plant material and ammonium chloride on the recovery of Rb^{86} from 9:1 ratios of sand to clays from Merrimac and Suffield soils, average of duplicate counts.

Treatment	Fractionation for recovery of Rb^{86} water-soluble %	"adsorbed"[1] %	"fixed"[2] %
Suffield clay, plant material, Rb^{86}	17.1	68.1	14.8
Suffield clay, NH_4Cl, Rb^{86}	73.4	16.3	10.3
Suffield clay, Rb^{86}	3.2	67.6	29.2
Merrimac clay, plant material, Rb^{86}	17.9	58.8	23.3
Merrimac clay, NH_4Cl, Rb^{86}	51.0	35.9	13.1
Merrimac clay, Rb^{86}	12.9	40.2	46.9

1 KOH treatment on steam bath 6 hours.
2 HF treatment 12 to 16 hours.